Statistical and Thermal Physics: Homework 8

Due: 18 February 2020

1 Changes in entropy for ideal gas processes.

A monoatomic ideal gas undergoes the process indicated on the PV diagram. The curved line is an isothermal compression. The initial process at volume V_i reduces the pressure to one quarter of P_i.

a) Determine the change in entropy, in terms of P_i and V_i, along the constant volume process.

b) Determine the change in entropy, in terms of P_i and V_i, along the constant pressure process.

c) Starting with the first law of thermodynamics and using the fundamental thermodynamic identity show that along an isothermal process

$$\mathrm{d}S = \frac{Nk}{V}\mathrm{d}V.$$

determine a general expression for the change in entropy for an isothermal process.

d) Determine the change in entropy, in terms of P_i and V_i, along the isothermal compression.

e) Determine the change in entropy for gas for the entire process.

f) Does the gas do work for the entire process? Is heat supplied to the gas for the entire process? Can this process occur so that the entropy of the system plus surroundings does not increase?
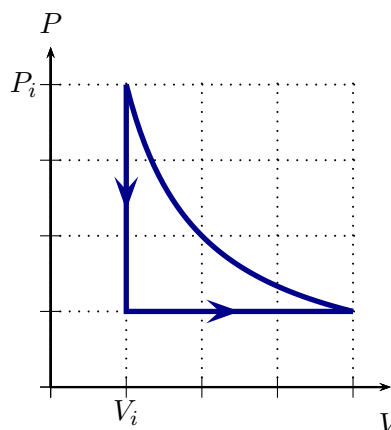
2 Gold immersed in water

A block of zinc with mass $0.750\,\mathrm{kg}$ is initially at temperature $120°\,\mathrm{C}$. The zinc is immersed in water with mass $1.25\,\mathrm{kg}$ and which is initially at temperature $20°$. The specific heat capacity of water is $4.186 \times 10^3\,\mathrm{J/kg\ K}$ and of zinc, $387\,\mathrm{J/kg\ K}$.

a) Determine the change in entropy of the zinc as it reaches equilibrium with the water.

b) Determine the change in entropy of the water as it reaches equilibrium with the zinc.

c) Determine the net change in entropy of the zinc and water.

3 Gould and Tobochnik, *Statistical and Thermal Physics*, 2.62, page 106.

4 System interacting with a heat bath

Consider a system with heat capacity C that interacts with a heat bath. Suppose that the system is initially at temperature T_{sys} and that the bath is a temperature T_B. The two are then placed in contact and during the process that follows the system remains at constant volume.

a) Show that the change in entropy of the system plus bath is

$$\Delta S = C \left[\ln \left(\frac{T_B}{T_{\text{sys}}} \right) + \frac{T_{\text{sys}}}{T_B} - 1 \right]$$

and note that this involves a function of the form

$$f(x) = \ln x + \frac{1}{x} - 1.$$

b) Determine when $f(x)$ attains a minimum and what this minimum is. Use this to describe the condition under which $\Delta S = 0$.

c) Use results from the previous part to describe whether the change in entropy is always positive when the bath is initially at a lower temperature than the system.

d) Use results from the previous part to describe whether the change in entropy is always positive when the bath is initially at a higher temperature than the system.

In all cases

$$Td S = \delta Q$$

a) At constant volume $\qquad \delta Q = C_v dT$

$$\Rightarrow \quad dS = \frac{C_v}{T} dT$$

Here $C_v = \frac{3}{2} Nk$

$$\Rightarrow \quad ds = \frac{3}{2} Nk \frac{dT}{T} \quad \Rightarrow \quad \Delta S = \frac{3}{2} Nk \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Rightarrow \quad \Delta S = \frac{3}{2} Nk \ln\left(\frac{T_f}{T_i}\right)$$

Now $\qquad \begin{rcases} P_i V_i = NkT_i \\ P_f V_f = Nk T_f \end{rcases} \Rightarrow \quad \frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = \frac{P_f}{P_i}$

Then $\qquad P_f = \frac{1}{4} P_i$

$$\Rightarrow \quad \boxed{\Delta S_1 = \frac{3}{2} Nk \ln\left(\frac{1}{4}\right)}$$

b) At constant pressure $\qquad \delta Q = C_p dT = \frac{5}{2} Nk\, dT$

$$\Rightarrow \quad dS = \frac{5}{2} Nk \frac{dT}{T}$$

$$\Rightarrow \quad \Delta S = \frac{5}{2} Nk \ln\left(\frac{T_f}{T_i}\right)$$

Again $\qquad \frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = 4 \qquad \Rightarrow \quad \boxed{\Delta S_2 = \frac{5}{2} Nk \ln(4)}$

c) $dE = TdS - PdV$

Then along an isothermal process $E = \frac{3}{2}NkT$ is constant

$\Rightarrow \quad dE = 0$

$\Rightarrow \quad TdS = PdV$

But $\quad P = \dfrac{NkT}{V}$

$\Rightarrow \quad TdS = \dfrac{NkT}{V}dV$

$\Rightarrow \quad dS = \dfrac{Nk}{V}dV$

$\Rightarrow \quad \Delta S = Nk\displaystyle\int \dfrac{dV}{V} = Nk \ln\left(\dfrac{V_f}{V_i}\right)$

d) For this process $\quad V_f = \frac{1}{4}V_i$

$\Rightarrow \quad \boxed{\Delta S_8 = Nk \ln\left(\dfrac{1}{4}\right)}$

e) $\Delta S_{tot} = \Delta S_1 + \Delta S_2 + \Delta S_3 = \frac{3}{2}Nk \ln\left(\frac{1}{4}\right) + \frac{5}{2}Nk \ln(4) + Nk \ln\left(\frac{1}{4}\right)$

$\Delta S_{tot} = \frac{5}{2}Nk\left[\ln\left(\frac{1}{4}\right) + \ln(4)\right]$

Then $\ln\left(\frac{1}{4}\right) = -\ln(4)$

$\Rightarrow \quad \boxed{\Delta S_{tot} = 0}$

f) Work is done on the gas since area under isotherm (positive) is greater than area under isobaric $\qquad W > 0$

Since $\Delta E = 0$ we have $\Delta E = W + Q \Rightarrow Q < 0$ (heat is removed)

No, the surroundings must absorb heat and since $TdS = \delta Q$ the change in entropy must be positive for surroundings

$$dS = \frac{\delta Q}{T}$$

$$\Rightarrow \quad \Delta S = \int \frac{\delta Q}{T}$$

We will need the equilibrium temperature. Then $Q_w + Q_{zn} = 0$

$$\Rightarrow C_w \Delta T_w + C_{zn} \Delta T_{zn} = 0$$

$$\Rightarrow C_w (T_f - T_{wi}) + C_{zn}(T_f - T_{zni}) = 0$$

$$\Rightarrow T_f (C_w + C_{zn}) = C_{zn} T_{zni} + C_w T_{wi}$$

$$\Rightarrow T_f = \frac{C_{zn} T_{zni} + C_w T_{wi}}{C_w + C_{zn}}$$

$$C_{zn} = 0.75 \, kg \times 387 \, J/kg \cdot K = 290 \, J/K \qquad\qquad T_{zni} = 393 K$$

$$C_w = 1.25 kg \times 4186 J/kg \cdot K = 5233 J/K \qquad\qquad T_{wi} = 293 K$$

$$T_f = \frac{290 J/k \times 393 K + 5233 J/k \times 293 K}{290 J/k + 5233 J/K} = 298 K$$

a) $$\Delta S_{zn} = \int_{T_i}^{T_f} \frac{C}{T} dT = C_{zn} \ln \frac{T_f}{T_i} = 290 J/k \ln\left(\frac{298K}{393k}\right) = -80.0 J/k$$

b) $$\Delta S_w = C_w \ln\left(\frac{T_f}{T_{wi}}\right) = 5233 J/k \ln\left(\frac{298}{293}\right) = 88.5 J/k$$

c) $$\Delta S = \Delta S_w + \Delta S_{zn} = 8.5 J/k$$

For the water
$$\Delta S_w = \int_{T_i}^{T_F} \frac{C_w \, dT}{T}$$

T_i → initial temp water

$$= C_w \ln T \Big|_{T_i}^{T_F} = C_w \ln\left(\frac{T_F}{T_i}\right)$$

Then $T_F = T_B$ = temp of bath ⟹ $\Delta S_w = C_w \ln\left(\frac{T_B}{T_i}\right)$

For the bath $\Delta S_B = \frac{Q_B}{T_B}$ where Q_B is heat gained by bath.

But $Q_B = -Q_{water}$ where Q_{water} is heated gained by water

$$Q_{water} = C_w (T_F - T_i) = C_w (T_B - T_i).$$

Thus $\Delta S_B = C_w \left(\frac{T_i}{T_B} - 1\right)$

Here $C_w = 4186 \text{ J/K}$

a) $T_i = 273 K$ $\qquad \Delta S_w = 4186 \text{ J/}_K \qquad \ln\left(\frac{363}{273}\right) = 1193 \text{ J/K}$

$T_B = 363 K$

$$\Delta S_B = 4186 \text{ J/}_K \left(\frac{273}{363} - 1\right) = -1036 \text{ J/K}$$

$\boxed{\Delta S_{total} = 157 \text{ J/K}}$

b) For first part $\Delta S = \Delta S_w + \Delta S_B = 4186 \text{ J/}_K \left[\ln \frac{318}{273} + \frac{273}{318} - 1\right] = 46.3 \text{ J/K}$

$T_B = 318 K$

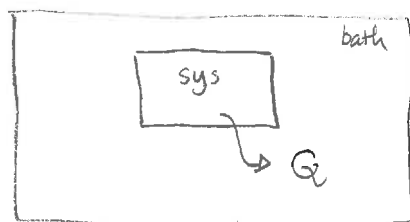For second part $\Delta S = 4186 \text{ J/}_K \left[\ln \frac{363}{318} + \frac{318}{363} - 1\right] = 35.10 \text{ J/K}$

$T_i = 318 K$

$T_B = 363 K$ ⟹ $\boxed{\Delta S \text{ for all} = 81.4 \text{ J/K}}$

c) Heat by bringing into contact with many heat baths at temps from 0°C → 90°C

a) The system undergoes a change from $T_{sys} \to T_B$ Then

$$\Delta S_{sys} = \int_{T_{sys}}^{T_B} \frac{\delta Q}{T} = \int_{T_{sys}}^{T_B} \frac{C\,dT}{T} = C \ln\left(\frac{T_B}{T_{sys}}\right)$$

The system acquires heat $Q = C(T_B - T_{sys})$. This happens at constant temperature. So

$$\Delta S_B = \frac{-Q}{T_B} = \frac{C(T_{sys} - T_B)}{T_B} = C\left(\frac{T_{sys}}{T_B} - 1\right)$$

Then the total change in entropy is:

$$\Delta S = \Delta S_{sys} + \Delta S_B \quad \Rightarrow \quad \Delta S = C\left[\ln\left(\frac{T_B}{T_{sys}}\right) + \frac{T_{sys}}{T_B} - 1\right]$$

b) $\frac{df}{dx} = \frac{1}{x} - \frac{1}{x^2} = \frac{1}{x^2}(x-1)$

and $\frac{df}{dx} = 0 \Rightarrow x = 1$. At this point $f(1) = 0$. Note that

$$\frac{d^2f}{dx^2} = -\frac{1}{x^2} + \frac{2}{x^3} = \frac{1}{x^3}(2-x) > 0 \quad \text{at } x=1. \text{ So}$$

$f(x)$ attains a minimum of 0 when $x=1$.

In this situation $\Delta S = Cf\left(\frac{T_B}{T_{sys}}\right)$ attains a minimum of $\Delta S = 0$ when $T_B = T_{sys}$.

c,d) Since $\Delta S = C f\left(\frac{T_B}{T_{sys}}\right)$ we know that $\Delta S = 0$ is a minimum regardless of T_B, T_{sys}